

## STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA



March 1, 1968

Quarterly Status Report No. 3  
SRI Project 6682  
Contract NASr-49(30)

RESEARCH RELATED TO MEASUREMENTS OF  
ATOMIC SPECIES IN THE EARTH'S UPPER ATMOSPHERE

GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) \_\_\_\_\_

Microfiche (MF) \_\_\_\_\_

Prepared for:  
National Aeronautics and Space Administration  
Office of Grants and Research Contracts, Code S ff 653 July 65  
Washington, D.C. 20546

N68-21318

FACILITY FORM 502

(ACCESSION NUMBER)

12

(PAGES)

01-94083

(NASA CR OR TMX OR AD NUMBER)

(THRU)

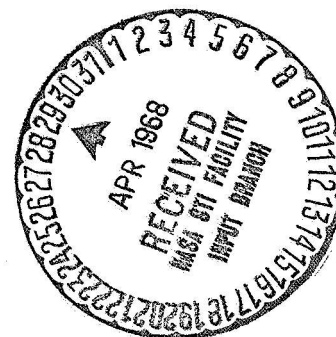
(CODE)

(CATEGORY)

By Bernard J. Wood

Approved:

Henry Wise, Chairman  
Department of Surface Science



## Introduction and Objective

Precise analysis by rocket- and satellite-borne mass spectrometers of the concentration of atomic oxygen in the earth's upper atmosphere is made difficult by the reactive character of the oxygen atoms themselves. These species can interact with solid surfaces by adsorption, by formation of oxides, and by catalytic production of molecular oxygen. Hence, the oxygen atom concentration as seen by a mass spectrometer may be substantially different from its real value in the environment due to atom removal on the various surfaces of the instrument. The objective of this project is to elucidate the kinetics and mechanisms that are associated with the interaction of oxygen atoms with solid surfaces of engineering interest under conditions similar to those encountered in the upper atmosphere.

The same difficulties in determining  $O/O_2$  ratios in the upper atmosphere are encountered in a laboratory experiment. The approach used in our study is to measure changes in oxygen atom concentration resulting from surface reaction and recombination in an environment in which changes in both the oxygen pressure and the rate of production of oxygen atoms are negligible. The theoretical basis of the experimental approach was described in detail in Quarterly Status Report No. 1 (September 1, 1967). Subsequent experiments with molecular oxygen, reported in Quarterly Status Report No. 2 (December 1, 1967), verified the general validity of the approach for measuring low-pressure gas/surface interaction kinetics.

## Experiments

The interaction of molecular oxygen with a platinum ribbon specimen has been studied further, because it has become evident that the chemical processes that occur during this interaction are quite pertinent to the problem of gaseous oxygen atom loss on metal surfaces. The constant-ambient pressure sorption measurements described in the preceding Quarterly Status Report have been extended and supplemented by flash

desorption determinations of the quantity and composition of desorbing gas.

The typical experimental procedure is outlined in Table I (refer to Fig. 1 for nomenclature of apparatus). This sequence of operations permitted quantitative measurement of:

1. the rate of sorption (or reaction) of oxygen with the surface
2. the total quantity of gas consumed by sorption (or reaction)
3. the total quantity and composition of the sorbed (or reacted) gas recovered by flash heating.

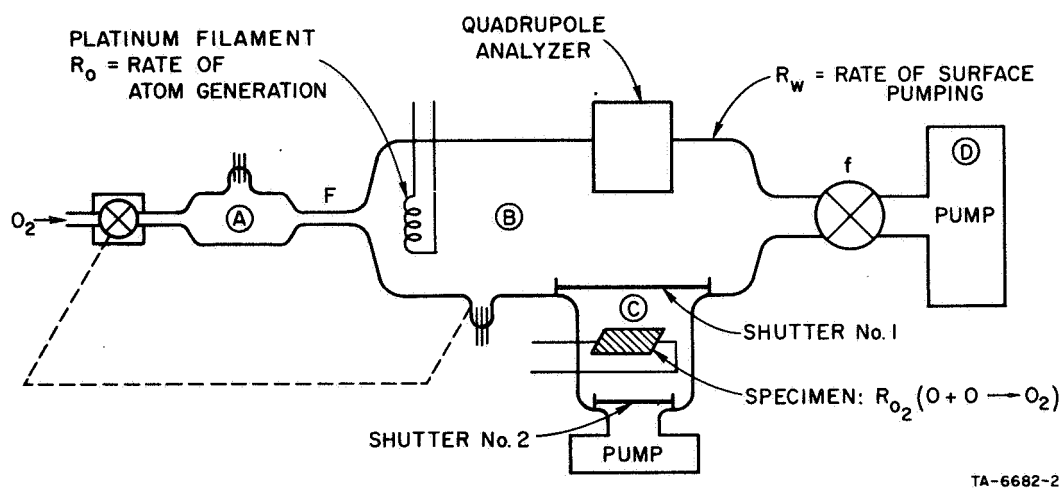
Parameters of significance which were varied are the temperature of the specimen during sorption (Step 5, Table I), the duration of the cleaning flash (Step 3), the residence time of the clean specimen in the system background gas prior to sorption (Step 4), and the oxygen pressure in the system during sorption (Step 5). A blank experiment, in which Steps 3 and 4 were omitted, showed that the wall of chamber C (Fig. 1) sorbs a negligible amount of oxygen relative to the platinum specimen.

It is important to note that under any of the conditions employed in these experiments, oxygen was never observed in the gas desorbed from the platinum ribbon. Indeed, when the ribbon was heated to flashing temperature in an atmosphere of oxygen, with steady-state gas flow through the system, the partial pressure of  $O_2$  diminished substantially to a new steady-state value. The two components observed by the quadrupole analyzer during flash desorption of the specimen were carbon dioxide and carbon monoxide. The former appeared when a cleaned specimen was first exposed to oxygen prior to flashing. The latter was liberated from the surface of a cleaned specimen which had resided for a time in the high-vacuum system at background pressures. The precise source of CO in the vacuum system is not clear, but the quadrupole analyzer indicates that the steady-state pressure of CO is  $P_{CO} \simeq 2 \times 10^{-9}$  torr.

Table I

## EXPERIMENTAL PROCEDURE

| Operation  | Inlet Valve | P <sub>B</sub><br>(torr) | P <sub>C</sub><br>(torr) | Shutter No. 1 | Shutter No. 2 | Specimen Temp. (°C) |
|--|-------------|--------------------------|--------------------------|---------------|---------------|---------------------|
| (1) Starting condition   | Closed      | $<5 \times 10^{-9}$      | $<5 \times 10^{-9}$      | Closed        | Open          | 25                  |
| (2) Inlet valve control set to admit O <sub>2</sub> and stabilize P <sub>B</sub>   | Open        | $1 \times 10^{-7}$       | $<5 \times 10^{-9}$      | Closed        | Open          | 25                  |
| (3) Specimen heated (cleaned)  | Open        | $1 \times 10^{-7}$       | peaks                    | Closed        | Open          | 840                 |
| (4) Specimen cooled  | Open        | $1 \times 10^{-7}$       | $<5 \times 10^{-9}$      | Closed        | Open          | 25                  |
| (5) Sorption commenced. Rate of sorption and quantity sorbed measured by recording P <sub>A</sub>  | Open        | $1 \times 10^{-7}$       | $1 \times 10^{-7}$       | Open          | Closed        | 25                  |
| (6) Sorption completed   | Open        | $1 \times 10^{-7}$       | $1 \times 10^{-7}$       | Open          | Closed        | 25                  |
| (7) System evacuated   | Closed      | $1 \times 10^{-8}$       | $1 \times 10^{-8}$       | Open          | Closed        | 25                  |
| (8) Specimen heated (desorbed). Total quantity of all gas desorbed evaluated from $\Delta P$ . Identity of gas established w/quadrupole analyzer | Closed      | peaks                    | peaks                    | Open          | Closed        | 840                 |
| (9) Specimen cooled  | Closed      | $1 \times 10^{-8}$       | $1 \times 10^{-8}$       | Open          | Closed        | 25                  |
| (10) Starting condition restored   | Closed      | $<5 \times 10^{-9}$      | $<5 \times 10^{-9}$      | Closed        | Open          | 25                  |



TA-6682-2

FIG. 1 SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

A heating time of 30 seconds was adopted as a standard cleaning flash for the specimen. By measuring the temperature of the central portion of the specimen with a Huggins Infrascopes radiation thermometer, it was determined that the ribbon attained a temperature within 5% of its steady-state maximum value of 840°C within 25 seconds after turning on the heating current. The pressure pulse associated with the cleaning flash was a sharp peak with a width of less than 10 seconds at the baseline. Longer periods of heating caused a subsequent slow rise in pressure which was attributed to degassing of the specimen leads (glass-covered kovar) and adjacent glass structures. It seemed reasonable to adjudge that the 30-second heating period produced an atomically clean specimen surface. Surface temperature measurements during the period following the 840°C cleaning flash showed that the specimen required 80 seconds to reach 200°C, the lower sensitivity limit of the Infrascopes. Hence a minimum cooling period of 120 seconds was allowed between cleaning and sorption, at which time the specimen temperature was assumed to be room-ambient (25°C).

The effects of the various parameters on the sorption/reaction characteristics of oxygen are summarized in Table II. It is of special interest that the total mass of gas sorbed as oxygen is generally about an order of magnitude more than the quantity of gas recovered as carbon dioxide during desorption.

### Discussion

Since the oxygen sorbed on the platinum specimen is not recovered as oxygen, there can be little doubt that chemical reaction occurs on the surface between the oxygen and the platinum or other sorbed materials. Based on the observed residual partial pressure of CO in the vacuum system as well as the identification of the desorbed gas as CO<sub>2</sub>, we conclude that a primary chemical process occurring on the surface is the catalytic oxidation of CO to CO<sub>2</sub>.

The disparity in the mass balance between sorbed and recovered gas (Table II) can be accounted for in large measure by proposing a second

Table II  
SORPTION/REACTION OF OXYGEN ON PLATINUM\*

| Specimen<br>Temp. During<br>Sorption<br>(°C) | PO <sub>2</sub> During<br>Sorption<br>(torr) | Residence Time<br>After Cleaning<br>(sec.) | Mass<br>Sorbed<br>(torr-ℓ x 10 <sup>6</sup> ) | Mass Desorbed (torr-ℓ x 10 <sup>7</sup> )<br>Total** AMU 28# AMU 44# |
|--|--|--|---|--|
| 25   | 5 x 10 <sup>-8</sup>                         | 120  | 2.3   | 1.5 -- --  |
|  | 1 x 10 <sup>-7</sup>                         | 120  | 2.3   | 1.5 -- 1.5   |
|  |  | 240  | 1.9   | 3.0 -- 4.5   |
|  |  | 600  | 1.6   | 2.3 -- 2.9   |
|  |  | 3000                                       | 0.61  | 2.2 16.0 --  |
|  |  | 300,000                                    | 0   | 8.3 ~20 --   |
| 200  | 1 x 10 <sup>-7</sup>                         | 120  | 3.5   | 0 -- 0   |
|  |  | 240  | 3.0   | 0 -- 0   |
|  |  | 360  | 4.1   | 0 0 --   |

\*Geometric surface area, 2.5 cm<sup>2</sup>.

\*\*Ion gage measurements.

#Values based on quadrupole analyzer calibration against ion gage with O<sub>2</sub>.

chemical reaction at the surface to form a platinum oxide (such as PtO or PtO<sub>2</sub>). Platinum oxides are known to be volatile<sup>1</sup> under the conditions of temperature and oxygen pressure employed in our experiments. Hence, it seems likely that upon heating, the fraction of the surface-sorbed oxygen which does not react with sorbed CO volatilizes as PtO or PtO<sub>2</sub>. These species would condense on adjacent cool surfaces and therefore would not be detected by the quadrupole analyzer, which in these experiments is outside of the line-of-sight of the specimen.

The diminution in mass of oxygen sorbed with increasing residence time of the cleaned specimen in the evacuated system suggests that CO sorption preempts sites that would otherwise be available for oxygen. Gaseous molecular oxygen apparently cannot react directly with the sorbed CO, for after extended periods of residence in the evacuated system, no oxygen sorbs, and the gas recovered upon flashing consists mainly of CO. The maximum quantity of gas sorbed under the conditions employed in these experiments corresponds to a surface coverage of less than 0.1 monolayer. On the freshly cleaned specimen (residence time <120 seconds) the sorbed layer likely consists in large measure of oxygen or a platinum oxide. On a specimen that has been exposed to the CO in the background gas for an extended time, the sorbed layer is carbon monoxide.

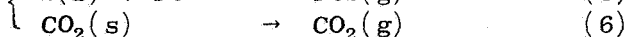
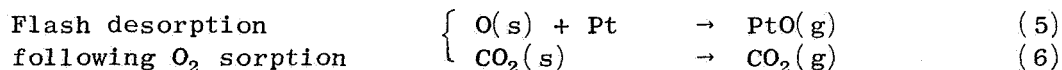
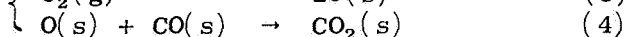
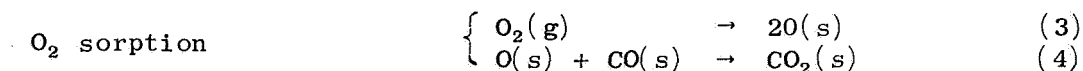
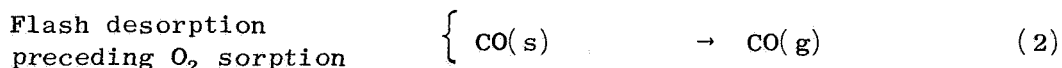
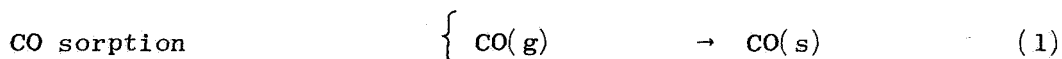
When the temperature of the specimen is maintained at 200°C, neither O<sub>2</sub>, CO, nor CO<sub>2</sub> is recovered by flash heating, yet more oxygen is consumed during sorption than at 25°C. This lends additional support to the existence of a stable platinum oxide which is volatile yet condensable, and further indicates that CO does not form a stable sorbed state on platinum at this temperature.

On the basis of these observations a mechanism may be postulated to describe the interaction of oxygen with a platinum surface:

---

<sup>1</sup>G. C. Fryburg and H. M. Petrus, J. Electrochem. Soc. 108, 496 (1961).





It is quite likely that gaseous atomic oxygen would participate in such a mechanism in a manner analogous to molecular oxygen as shown in Eq. (4) above. As a matter of fact the chemisorption of O would not require the activated process given by Eq. (3). An additional step that might be involved in an atmosphere containing atomic oxygen would be



If there were a source of CO to replenish CO(s), Eq. (7) would represent an effective sink for gaseous oxygen atoms which would compete with the recombination process:



Effective sources of CO could be a residual partial pressure of the gas in the sampling chamber or dissolved carbon impurity in the metal.

In view of the results of a number of recent rocket-borne mass spectrometer investigations of the upper atmosphere,<sup>2</sup> it is quite possible that reactions (4) and (7) comprise the principal loss mechanism for atomic oxygen in such experiments. The data of Hedin and Nier,<sup>3</sup> which was obtained from a rocket carrying three mass spectrometers with

---

<sup>2</sup>U. von Zahn, J. Geophys. Res. 72, 5933-37 (1967).

<sup>3</sup>A. E. Hedin and A. O. Nier, J. Geophys. Res. 71, 4121-31 (1966).

different ion-source geometries, showed that 99% of the incident atomic oxygen was lost when the ion source was effectively shielded with a metal plate. However, no enhancement in the intensity of mass 32 was reported, which suggests that the loss mechanism was not an atom recombination reaction.

In an earlier flight,<sup>4,5</sup> Nier and his associates observed that mass 44 was a major peak reported by their open-source mass spectrometer, and that the ratio (mass 44/mass 16) remained approximately constant during the flight (Cf. Fig. 6 in Ref. 4 and Fig. 6 in Ref. 5). These authors pointed out that at the apex of the flight (209 km) an appreciable fraction of the mass 28 peak was associated with CO. Based on these observations, it seems likely that the catalytic oxidation of CO to CO<sub>2</sub> (Eq. 7) is a significant if not the principal loss mechanism for atomic oxygen in mass spectrometric analyses of the upper atmosphere.

The possibly dominant role of sorbed CO in oxygen-surface interactions endows selective CO getters such as gold with special interest. Although gold is known to sorb CO selectively and tenaciously, the behavior of the CO-saturated surface in contact with atomic or molecular oxygen has not been investigated. The further fact that gold has been proposed as a surface coating for metal parts in the sampling and source regions of a future OGO mass spectrometer renders particularly interesting and pertinent an investigation of oxygen interaction with this metal. Hence, gold has been selected as the specimen of interest for further studies in our laboratory.

The problem of atom generation in the vacuum system remains. The use of ozone as a source of atomic oxygen proved unsuccessful (Cf. Monthly Progress Report No. 8, February 1, 1968). The use of a heated

---

<sup>4</sup>A. O. Nier, J. H. Hoffman, C. Y. Johnson, and J. C. Holmes, J. Geophys. Res. 69, 979-89 (1964).

<sup>5</sup>A. O. Nier, J. H. Hoffman, C. Y. Johnson, and J. C. Holmes, J. Geophys. Res. 69, 4629-36 (1964).

tungsten filament in an appropriately cooled chamber presently seems to be the most promising technique for establishing an enhanced steady-state partial pressure of oxygen atoms in the vacuum system. Hence, when the system is next opened to insert a gold specimen, a tungsten filament furnace as a source of oxygen atoms will also be installed. The design of this furnace is basically simple, and no major changes in the configuration of the apparatus will be required to accommodate it. Therefore, the interaction of both molecular and atomic oxygen may be investigated by the procedures developed.

#### Personnel

Personnel participating in this project during this quarter include Noboru Endow, Henry Wise, and Bernard J. Wood.